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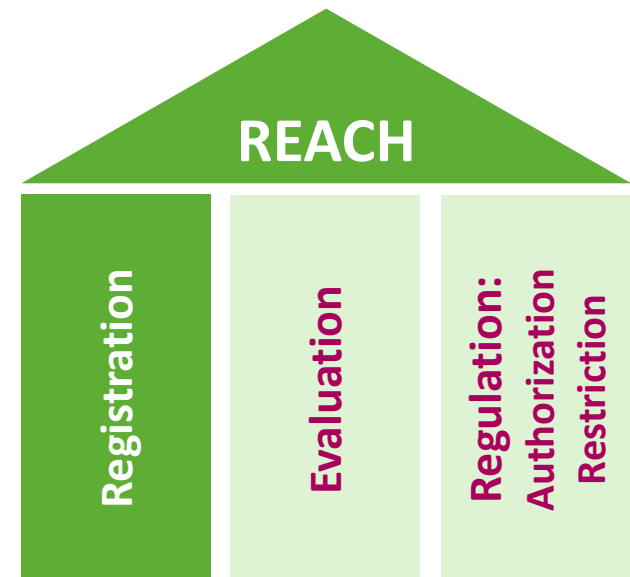
Regulation needs support from research: Short-chain PFASs under REACH

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Section IV 2.3 – Chemicals
German Environment Agency (UBA), Germany

REACH - Registration, Evaluation, Authorisation and Restriction of Chemicals

*“Article 1(1): The purpose of this Regulation is to ensure **a high level of protection of human health and the environment** [...] as well as the free circulation of substances on the internal market while **enhancing competitiveness and innovation.**” (EC 1907/2006)*

- Companies: Production and placing on the market of substances in the EU only when registered under REACH → **no data no market!**
- Authorities: Different instruments to evaluate chemicals and to initiate risk management measures
 - Substances of very high concern (SVHC)
 - Authorization
 - Restriction



<http://echa.europa.eu/web/guest/information-on-chemicals/registered-substances>

Outline

- **Current regulatory status of long-chain PFASs under REACH**
- **Concerns on short-chain PFASs and research needs**
- **Regulatory activities on short-chain PFASs under REACH**

Current regulatory status of long-chain PFASs under REACH

Substances of very high concern (SVHC) listed on Candidate List

C₁₁ – C₁₄ perfluoroalkyl carboxylic acids (PFCAs)

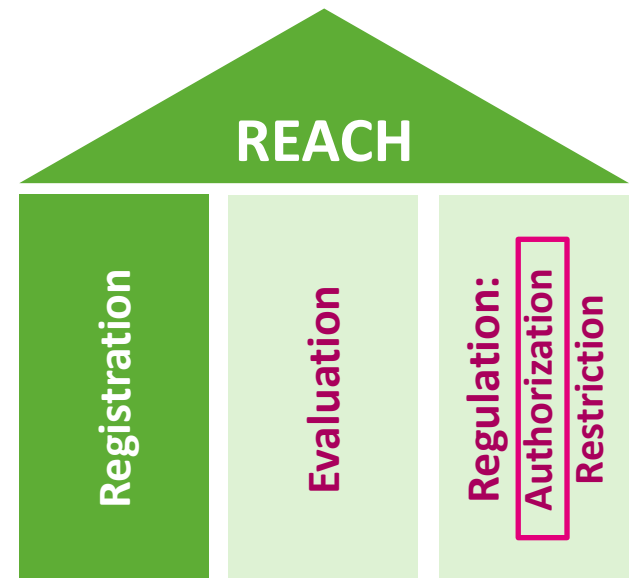
listed as very persistent, very bioaccumulative (vPvB)

C₈ – C₁₀ PFCAs (PFOA, PFNA, PFDA)

listed as persistent bioaccumulative and toxic (PBT)

C₆ PFSA (PFHxS)

listed as vPvB



<http://echa.europa.eu/candidate-list-table>

Current regulatory status of long-chain PFASs under REACH

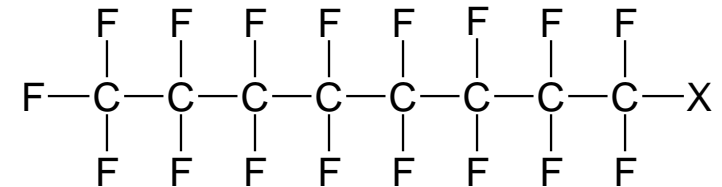
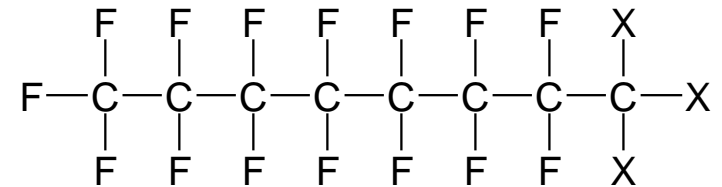
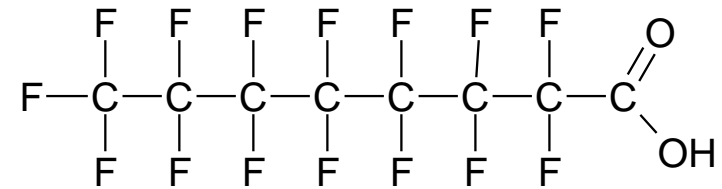
Restriction of PFOA, its salts, and related substances

COMMISSION REGULATION (EU) 2017/1000

of 13 June 2017

- Manufacturing or placing on the market prohibited
- Use and placing on the market in another substances, as a constituent, in a mixture and an article prohibited above the following concentration limits:
 - 25 ppb of PFOA including its salts
 - 1000 ppb of one or a combination of PFOA-related substances
- From 2020 on
- Longer transition periods or derogations for several uses

(<http://www.reach-info.de/pfoa2.htm>)



Exceptions:

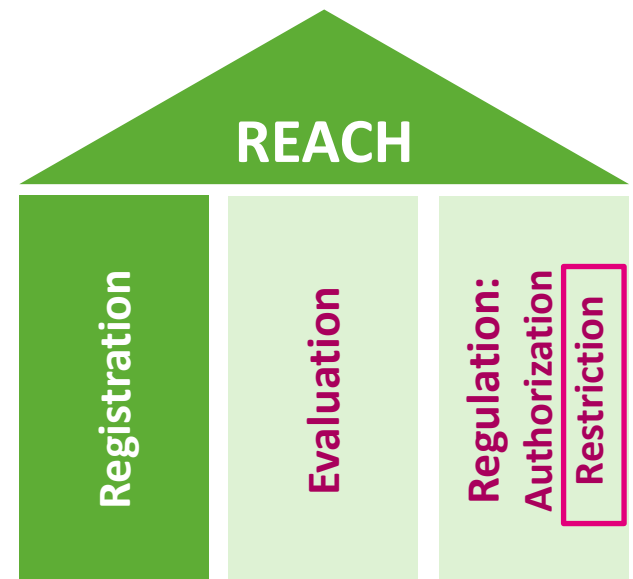
$\text{C}_8\text{F}_{17}\text{-X}$, where X= F, Cl, Br.

$\text{C}_8\text{F}_{17}\text{-C(=O)OH}$, $\text{C}_8\text{F}_{17}\text{-C(=O)O-X'}$, $\text{C}_8\text{F}_{17}\text{-CF}_2\text{-X'}$
(where X'= any group, including salts)

Current regulatory status of long-chain PFASs under REACH

Restriction of C₉-C₁₄ PFCAs, their salts and related substances

→ to be submitted in 2017 by Sweden and Germany



<http://echa.europa.eu/addressing-chemicals-of-concern/restrictions/list-of-restrictions>

Shift from long-chain to short-chain PFASs

For the majority of known uses of long-chain PFASs, short-chain PFASs as alternatives are available



Source: (1) Jürgen Fälchle (2) Norman Chan, (3) industrieblick, (4) Stillfx, (5) Luisa Leal, (6) Kzeno, (7) demarco, (8) Tobilander/Fotolia.com

Outline

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- **Concerns on short-chain PFASs and research needs**
- **Regulatory activities on short-chain PFASs under REACH**

Terminology short-chain PFASs

Perfluoroalkyl sulfonic acids (PFSA) < 6 fully fluorinated C-atoms
Perfluoroalkyl carboxylic acids (PFCA) < 7 fully fluorinated C-atoms
and their precursors

Concerns on short-chain PFASs – Overview

Short-chain PFASs

Persistent

- Based on read-across from long-chain PFASs
- Long-range transport and findings in remote areas

Mobility and exposure of organisms

- Potential to contaminate drinking water resources
- Difficult to be removed from water
- Binding to proteins
- Non-negligible half-lives in organisms
- Enrichment in plants

Toxic

- No indications for ecotoxicity
- Toxicity to humans to be assessed
- Potential endocrine disruptors

Representatives of European Authorities agreed: properties are of concern (UBA-Workshop in October 2016)

BUT non-classical combination of concerns so far not covered by REACH

→ **regulatory activities under development**

→ **more scientific knowledge would be helpful to eliminate data gaps**

Concerns on short-chain PFASs – High mobility

- Short-chain PFASs can occur in raw water and can therefore be found in drinking water
- Short-chain PFASs cannot be eliminated from water with the commonly applied measures (e. g. Lundgren et al. 2014)



Emotion\fotolia.com

Potential exposure of humans via drinking water

See also presentation from Michael Neumann on persistent, mobile and toxic (PMT) substances under REACH

Examples:

- 18% of 85 Spanish tapwater samples (Gellrich et al., 2013)
- 23% of 26 German tapwater samples (Llorca et al., 2012)
- 86% of 7 tapwater samples from six EU Countries (Ullah et al., 2011)
- 49% of 26 waterworks along the river Rhine (Wilhelm et al., 2010)

Concerns on short-chain PFASs – Enrichment in plants

- Plant uptake shown by several studies e.g. for wheat, maize, grass and vegetables
- Enrichment in edible parts of plants
- Benchmarking with PFOA: PFHxA higher uptake and higher transfer to edible parts of plants

(Felitzeter et al. 2014; Krippner et al. 2015; Wen et al. 2014; Yoo et al. 2011)

**Potential exposure of
humans via food**



Source: Marc Rathman\ fotolia.de

Concerns on short-chain PFASs – Exposure of organisms

- REACH criterion for bioaccumulation based on the bioconcentration factor is not fulfilled (Martin et al. 2003)
- Half-lives in organisms including humans range from a few hours to a few days (e. g. Chengelis et al., 2009; Gannon et al., 2011; Numata et al., 2014; Russell et al. 2013)
- Binding to proteins (Bischel et al. 2011)
- Occurrence in humans (e. g. Lee and Mabury 2011)
- Unclear whether short-chain PFASs bioaccumulate

**Sufficient exposure durations for
provoking adverse effects in
organism**



Tomasz Trojanowski/Fotolia.com

Concerns on short-chain PFASs

- Persistent in the environment
 - High mobility: Potential exposure of humans via drinking water
 - Enrichment in plants: Potential exposure of humans via food
- Permanent and non-reversible exposure of organisms
- Exposure of organisms: Sufficient for provoking adverse effects in organism

What will happen in the long-term? Predictions needed!

- Background concentrations
- Effects on human health

Knowledge on uses and emissions needed

Regulatory activities on short-chain PFASs

Restriction

Denmark: Polyfluorinated silanes in mixtures containing organic solvents in spray products
→ currently under discussion by REACH committees

Substance evaluation

- 2013 Precursors of C₇ PFCA by Belgium and the Netherlands
- 2016 6:2 FTA and 6:2 FTMA (precursors of C₆ PFCA (PFHxA)) by Germany
- 2017 Five PFOA-Alternatives (ADONA, GenX, ...) by Germany
- 2018 C₄ PFAS precursors by Germany

Risk Management Option (RMO) Analysis

- C₄ PFSA (PFBS) by Norway
- C₆ PFCA (PFHxA) and related substances by Germany

Conclusion

Long-chain PFASs under REACH

- $C_8 - C_{14}$ PFCAs and PFHxS are listed as substances of very high concern
- PFOA and related substances are restricted
- Restriction for $C_9 - C_{14}$ PFCAs and related substances is under preparation

Short-chain PFASs under REACH

- Properties of short-chain PFASs are of concern but they differ from “classical PBT-substances”
- Activities under REACH are ongoing to address these concerns
- **More scientific knowledge would be helpful**
 - on long-term trends and potential effects
 - on uses and emissions

Thank you for your attention!

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IV 2.3 Chemicals

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www.uba.de/themen/chemikalien/chemikalien-reach/stoffgruppen/per-polyfluorierte-chemikalien-pfc

www.reach-info.de/pfc.htm

[http://www.umweltbundesamt.de/publikationen/understanding-the-exposure-pathways-of-per-and-polyfluoralkyl-substances \(PFASs\)](http://www.umweltbundesamt.de/publikationen/understanding-the-exposure-pathways-of-per-and-polyfluoralkyl-substances-(PFASs))

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Current status of CLP regulation on long-chain PFASs

PFOS and its Li, Na, NH₄, diethanolamine salts – listed in Annex VI



- Carcinogenicity, **Reproductive toxicity** including lactational exposure, Specific target organ toxicity, Acute toxicity, Aquatic chronic toxicity



PFOA – listed in Annex VI

- Carcinogenicity, **Reproductive toxicity** including lactational exposure, Specific target organ toxicity, Acute toxicity, Serious eye damage/ Eye irritation

PFNA – listed in Annex VI

- Carcinogenicity, **Reproductive toxicity** including lactational exposure, Specific target organ toxicity, Acute toxicity, Serious eye damage/ Eye irritation

PFDA – listed in Annex VI

- Carcinogenicity, **Reproductive toxicity** including lactational exposure

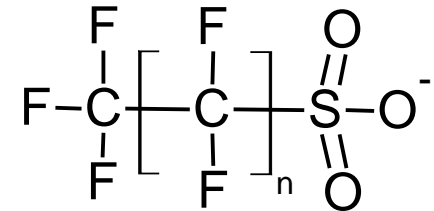
Terminology - PFASs

Fully or partly fluorinated carbon chain connected to a functional group

Perfluoroalkyl sulfonic acids (PFSAs)

long-chain ≥ 6 fully fluorinated C-atoms, e.g. PFOS

short-chain < 6 fully fluorinated C-atoms, e.g. PFBS



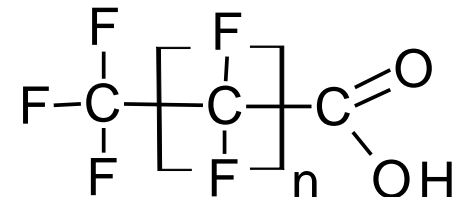
Perfluoroalkyl carboxylic acids (PFCAs), e.g. PFOA

long-chain ≥ 7 fully fluorinated C-atoms, e.g. PFOA

short-chain < 7 fully fluorinated C-atoms, e.g. PFBA, PFHxA

Precursors of PFSAs and PFCAs, e.g.

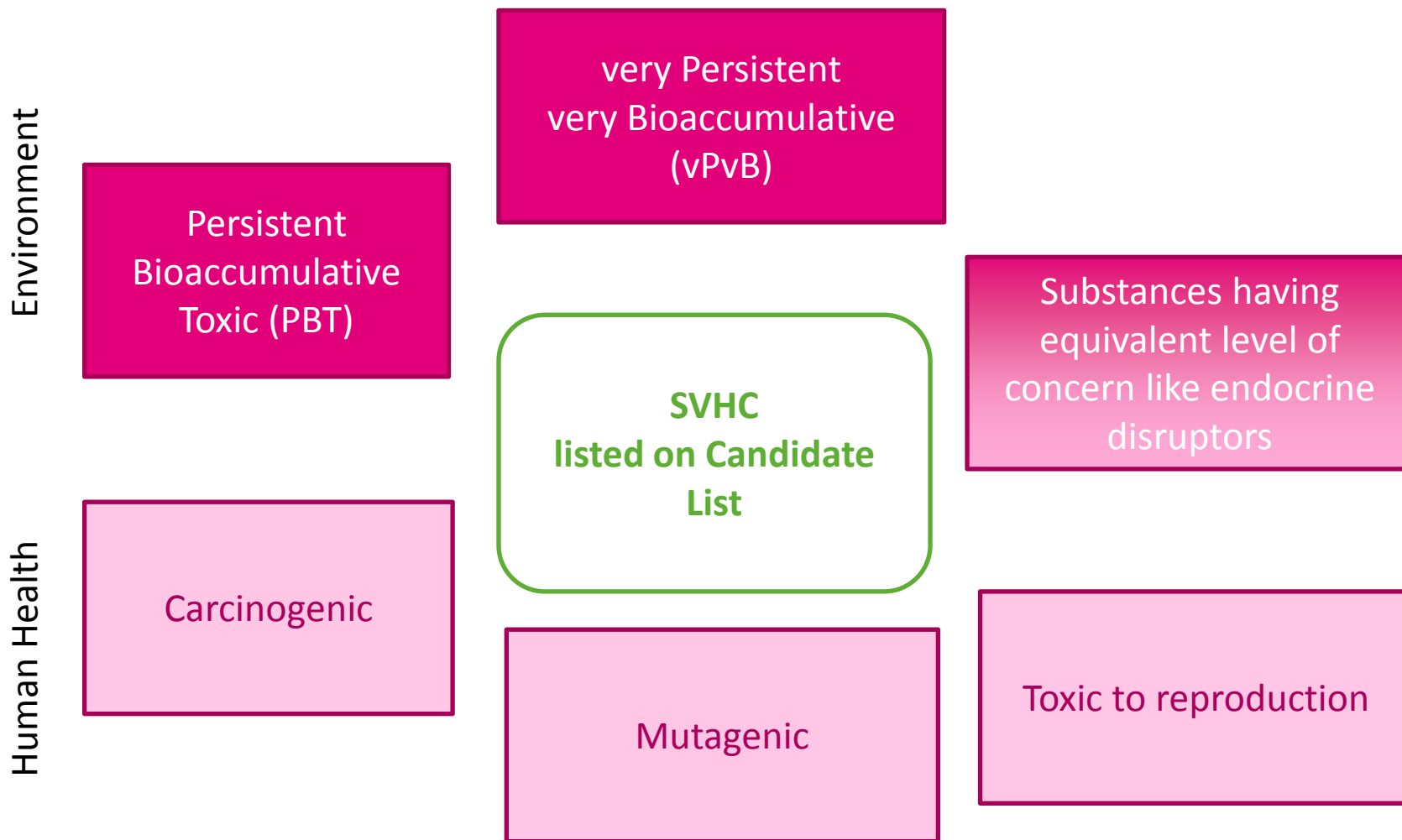
Fluorotelomer alcohols (FTOHs), e.g. 8:2 FTOH



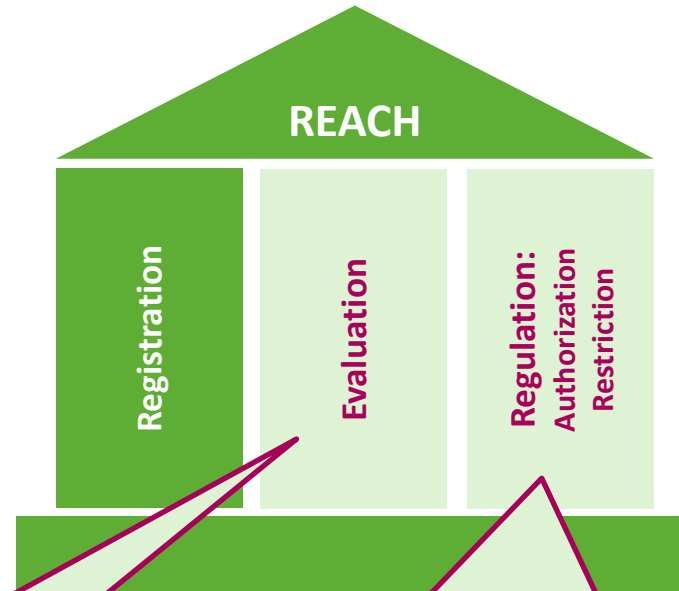
Fluorinated polymers: Polymers with fluorinated side-chains

Fluoropolymers: Polymers with fluorinated backbone

Substances of very high concern (SVHC)



REACH instruments



- Substance evaluation
- Dossier evaluation

- Substances of very high concern (SVHC)
- Authorization
- Restriction

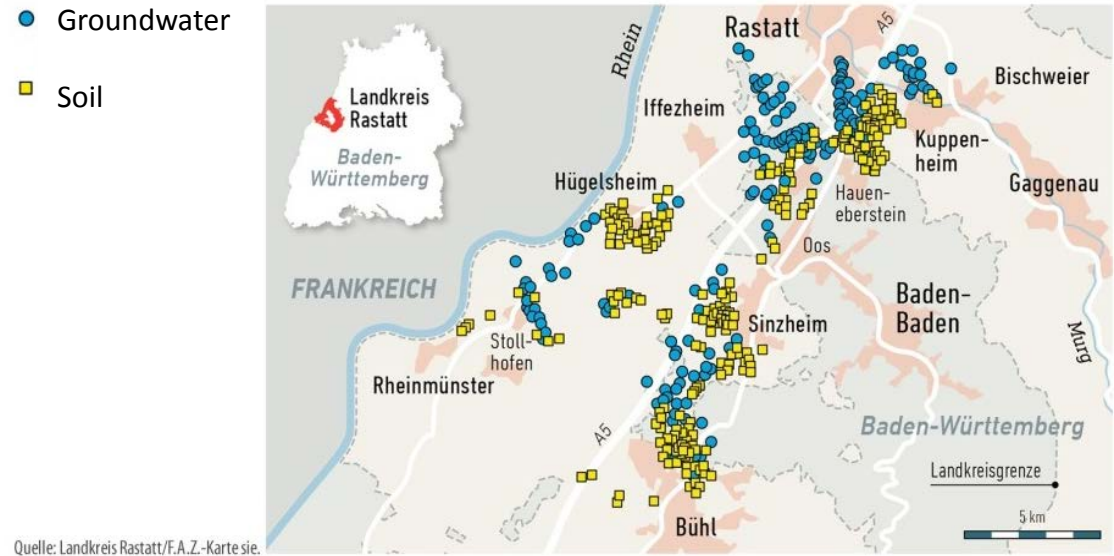
=> Risk management option analysis (RMOA)

Concerns on short-chain PFASs – Rastatt case in Germany

- PFASs-polluted fertilizer
- 400 ha contaminated agricultural area
- Occurrence of short- and long-chain PFASs in soil and groundwater
- Enrichment of short-chain PFASs in plants
- Contaminated drinking water
- 2 closed water works
- Agricultural production stop in highly contaminated areas
- Remediation seems not possible (technologies, costs, responsibilities)

Monitoring stations showing PFASs contamination

- Groundwater
- Soil



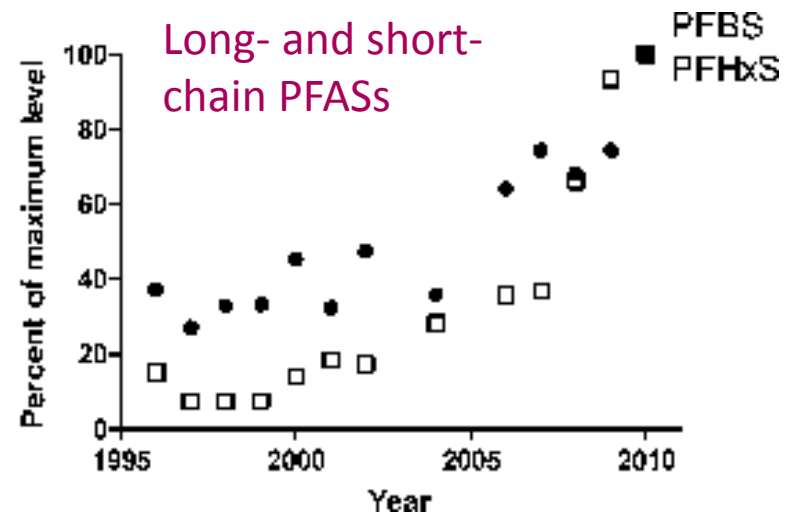
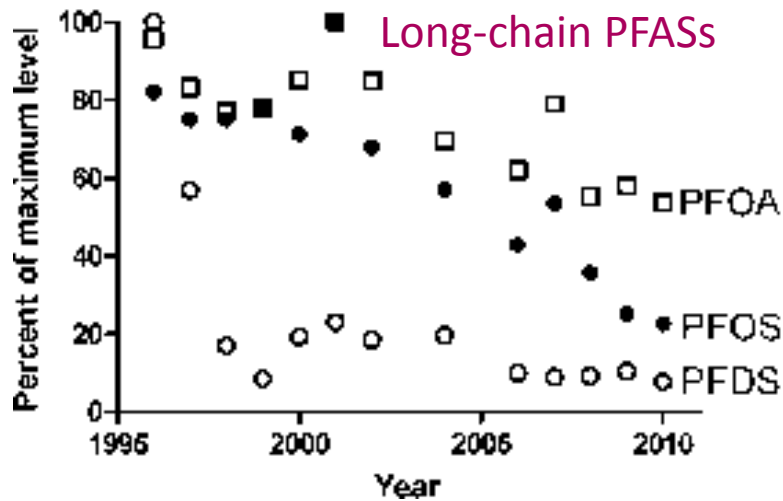
Source: Marc Rathman\ fotolia.de

Concerns on short-chain PFASs – Uppsala case in Sweden

- Polluted fire-fighting training site
- Contamination of aquifer with short-chain and long-chain PFASs over 20 years
- Contamination of drinking water
- Occurrence of PFASs in human blood



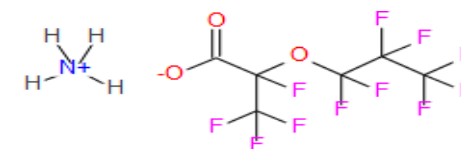
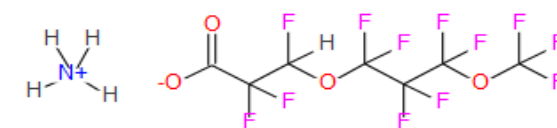
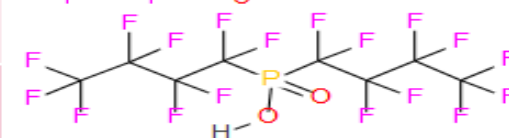
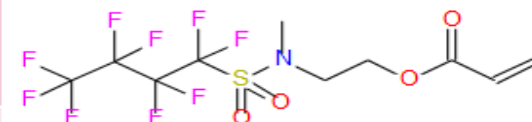
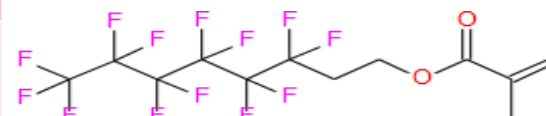
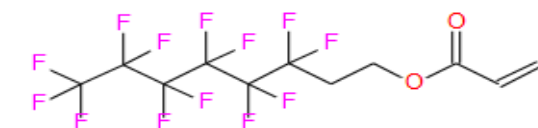
Source: Thomas Brugger/fotolia.com



Temporal trends of PFASs in blood of primiparous women in Uppsala, Glynn et al. 2012

REACH Substance Evaluations 2016-2018

Name	EC-Nummer
3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl acrylate	241-527-8
3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl methacrylate	218-407-9
2-[methyl[(nonafluorobutyl)sulphonyl]amino]ethyl acrylate	266-733-5
bis(nonafluorobutyl)phosphinic acid	700-183-3
(WÄSSRIGE LOESUNG DES MV31-KALIUMSALZ)	444-340-1
ammonium 2,2,3-trifluoro-3-(1,1,2,2,3,3-hexafluoro-3-trifluoromethoxypropoxy)propionate	480-310-4
Ammonium 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoate	700-242-3
ammonium difluoro[1,1,2,2-tetrafluoro-2-(pentafluoroethoxy)ethoxy]acetate	700-323-3
Polyfluoro-5,8,11,14-tetrakis(polyfluoralkyl)-polyoxaalkane	



<http://echa.europa.eu/information-on-chemicals/evaluation/community-rolling-action-plan/corap-table>
<http://echa.europa.eu/information-on-chemicals/registered-substances>